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(54) **Jet printing ink compositions and method for their production.**

(57) A jet printing ink composition includes a sufficient quantity of a secondary amine (selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, and dibutyl amine) to inhibit the corrosiveness of the composition without adversely affecting its printing characteristics. In a method for producing a jet printing ink composition the corrosiveness of the composition is reduced by adding a sufficient quantity of such a secondary amine. The invention simplifies the formulation of jet printing ink compositions by providing a means for inhibiting the corrosiveness of the composition without adversely affecting its printing characteristics, and similarly improves existing formulations. Jet printing machines using such ink compositions are less susceptible to wear and/or damage through corrosion of those metal components exposed to the jet printing ink.

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This invention relates to jet printing ink compositions and their production.

Ink jet printing is a well-known technique by which printing is accomplished without contact between the printing device and the substrate on which the printed characters are deposited. This technique of non-contact printing is particularly well suited for application of characters onto irregularly shaped surfaces including, for example, the bottom of beverage containers.

In one technique for performing ink jet printing, a stream of droplets of ink are projected toward a surface and the trajectories of the droplets are controlled electronically so that the droplets are caused to form the desired printed image on a relatively movable substrate. Another technique of ink jet printing is to direct droplets on demand from a set of orifices at a relatively moving substrate.

In general, ink jet printing techniques impose rigid requirements on the ink composition. To be suitable for use as a jet ink, a composition must meet some or all of the requirements of viscosity, resistivity, solubility, compatibility of components and wetability of the substrate. Further, the ink must be quick drying and smear resistant and capable of passing through the ink jet nozzle without clogging. The ink should also permit rapid clean-up of the machine components with minimum effort.

Corrosion of metal parts is a problem presented in many industrial fields, including the field of ink jet printing. Heretofore, it has been difficult to develop jet printing ink compositions which do not promote undue corrosion of metal parts of the ink jet printing apparatus with which the printing ink comes into contact. Frequently it has been necessary to expend substantial time and effort in formulating each particular ink jet formulation to render the same acceptable from the standpoint of minimizing metal corrosion.

A need has therefore existed for a corrosion inhibitor which could be incorporated into non-aqueous liquids, such as jet printing ink compositions, to reduce corrosion of metal parts coming into contact with the ink composition whilst not adversely affecting the properties of the ink composition. Jet printing ink compositions must meet very specific, stringent requirements with respect to many particular physicochemical properties, such as electrical conductivity, sonic velocity, viscosity, and the like. If a corrosion inhibitor has an effect on any such property, it may render the jet printing ink composition unworkable, without reformulation, requiring the expenditure again of large quantities of time and effort.

For general applications in fields not requiring such stringent control of physicochemical parameters, many compositions, including dialkyl amines and derivatives and salts thereof, have been employed as corrosion inhibitors. For example, U.S. Patent No. 4,975,211 discloses the use of diethylamine complexes of borated alkyl catechols as corrosion inhibitors in lubricating oils. Amine-complexed zinc salts of organic diacids, employing compounds such as zinc dibasate diethylamine, are disclosed in U.S. Patent No. 4,774,345. U.S. Patent No. 4,748,011 discloses the use of amines such as diethylamine and dipropylamine as corrosion inhibitors in natural gas formulations. U.S. Patent No. 4,744,913 discloses the use of dipropylamine and dibutylamine as corrosion inhibitors in de-icing and anti-icing agents for aircraft. U.S. Patent No. 4,698,279 discloses the use of diisopropylamine in a back coating layer of magnetic recording tape, to improve the resistance of the magnetic layer to corrosion.

Diisopropylamine nitrite is disclosed as a corrosion inhibitor in a rust preventative, in U.S. Patent No. 4,677,177. Organic phosphate adducts with diethylamine are discussed in U.S. Patent No. 4,584,175 as extending corrosion protection to magnesium and its alloys, used in a plastic sheet for enveloping metal objects to be protected. U.S. Patent No. 4,501,674 discloses the use of diethylamine as an ancillary agent for use in an enzyme system for reducing corrosion, when used in combination with crude oil additives. Diethylamine is also included in an absorption refrigeration system, as shown in U.S. Patent No. 4,455,247. U.S. Patent No. 4,433,127 shows room temperature curable silicon compositions which are effective for protecting copper and other metals from corrosion, the composition optionally containing dibutylamine.

U.S. Patent No. 4,342,596 discloses the use of diisopropylamine in a metal-corrosion inhibiting composition for use as a non-petroleum based metal corrosion inhibitor. Diisopropylamine is also used in cooling water, as disclosed in U.S. Patent No. 4,338,209, in combination with the metal corrosion inhibitor disclosed in that patent. U.S. Patent No. 4,295,979 discloses the use of diethylamine as an activator which is believed to be incorporated into alkyl polysulfide used in corrosion inhibitors for gas wells. Diisopropylamine nitrite is again employed as a volatile corrosion inhibitor used in the manufacture of corrosion resistance ferromagnetic metal powders, in accordance with U.S. Patent No. 4,253,886. U.S. Patent No. 4,204,972, referring to published German application No. 2,532,228 simply states that dialkylamines such as dibutylamine are known to inhibit corrosion.

The use of disubstituted lower alkyl amines in carbon dioxide propellants, as corrosion inhibitors, is discussed in U.S. Patent No. 4,161,458. The use of amines such as diethylamine, dipropylamine, and the like in forming certain corrosion inhibiting salts is discussed in U.S. Patent No. 4,101,328. Ball point pen inks containing diethylamine salt as a corrosion inhibitor is disclosed in U.S. Patent Nos. 4,077,807 and

4,077,727. U.S. Patent No. 3,964,927 discloses the use of dibutylamine as a corrosion inhibitor in an electrolyte used in a lead dioxide-zinc rechargeable-type cell and battery. Dibutylamine pyrophosphate is employed as a corrosion inhibitor in an aqueous system, as disclosed in U.S. Patent No. 3,935,125. U.S. Patent No. 3,925,223 discloses the use of dipropylamine and dibutylamine as corrosion inhibitors in hydraulic fluids. Diisopropylamine nitrite is disclosed as a corrosion inhibitor used in corrosion inhibiting paper in U.S. Patent No. 3,891,470.

Despite all of the foregoing uses of dialkyl amines, such as diethyl amine, dipropyl amine, and dibutyl amine, in corrosion inhibiting formulations, either directly, or as salts, derivatives, or complexes, over many years, such amines have never been employed for purposes of corrosion inhibition in ink jet formulations.

As a result of extensive research we have found that if diethyl amine, dipropyl amine, diisopropyl amine, or dibutyl amine is incorporated into non-aqueous jet printing ink compositions, such amine may surprisingly be introduced at a level sufficient to inhibit corrosion of metal such as stainless steel placed in contact with the jet printing ink composition, whilst surprisingly having essentially no effect upon the physicochemical properties of the jet printing ink composition. The ability to add such amines in sufficient quantity to inhibit corrosion, whilst not significantly affecting the physicochemical properties of the jet printing ink composition, is of great importance as it allows previously formulated jet printing ink compositions to be rendered corrosion resistant without the need of totally reformulating the ink composition.

According to one aspect of the present invention, a jet printing ink composition includes a sufficient quantity of at least one dialkylamine (that is a secondary amine) selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, or dibutyl amine to inhibit the corrosiveness of the composition without adversely affecting the printing characteristics of the composition.

According to another aspect of the present invention, a jet printing ink composition comprises a carrier and a colourant that is soluble or dispersable in the carrier and includes a sufficient quantity of at least one secondary amine selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, and dibutyl amine to reduce the corrosiveness of the composition.

According to a further aspect of the present invention, a method of producing a jet printing ink composition includes reducing the corrosiveness of the composition by adding a quantity of at least one secondary amine selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, and dibutyl amine, and the quantity of added secondary amine is insufficient adversely to affect the printing characteristics of the composition.

As indicated, the present invention provides a jet printing ink composition that has a reduced tendency to promote corrosion of metal that comes into contact with the composition. By use of the specific secondary amine corrosion inhibitors, it is possible to leave unaffected the beneficial properties of the ink jet ink formulation, such as adhesion and drying time of the ink. Also, the corrosion inhibitors of use in the present invention do not destabilize the ink, as they do not substantially affect the critical physicochemical properties of the jet printing ink formulation.

Thus, a normally corrosive ink jet ink formulation may be rendered less corrosive, or essentially noncorrosive, by adding a corrosion reducing amount of a secondary amine selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, dibutyl amine, or mixtures thereof. By use of such secondary amines in the jet printing ink composition, corrosion of the metal parts of an ink jet printing apparatus that are susceptible to corrosion, due to exposure to chloride from components of the composition such as dyes or electrolytes, is reduced or eliminated. Typically, the amount of secondary amine present in the ink formulation will be from about 0.1 to about 10.0 percent, based upon the total weight of the ink formulation, preferably from about 0.5 to about 2.0 percent, and most preferably from about 1.0 to about 1.5 percent.

The jet printing ink composition preferably includes a carrier and a colourant that is soluble or dispersable in the carrier. Typically the colourant will be a dye or a pigment.

The jet printing ink composition may also contain a resin binder component such as a vinyl acetate copolymer to improve adhesion between the printed image and the substrate on which the printing is effected. A variety of such resin binders may be employed, as described in U.S. Patent Nos. 4,210,566, 4,260,531, 4,567,213 and 4,070,322, all of which are incorporated by reference. Useful resin binders include resins that are soluble in the carrier.

Preferable resin binders include those having pendant amino groups, such as those disclosed in U.S. Patent No. 4,834,799, which is also incorporated by reference. One resin useful in ink jet ink formulations is sold under the trademark JONCRYL , which is a copolymer of a methacrylic or acrylic ester and acrylic acid.

The amount of resin binder in the compositions of the present invention is not critical and may be varied from about 5 to about 20 percent, by weight, based upon the total weight of the composition.

Preferably, the amount of resin binder will be from about 9 to about 12 percent and most preferably from about 9 to about 10 percent.

A variety of carriers may be utilized. The carrier is not critical so long as it is capable of dissolving or dispersing the colourant and dissolving the binder resin, if present. One principal carrier is typically a mixture of a lower alcohol and a lower ketone, each preferably having no more than 10 carbon atoms. An alcohol which typifies those that are useful is methyl alcohol. Useful ketones in the present invention include aliphatic ketones having no more than 10 carbon atoms, in straight or branched chain arrangement, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or an alicyclic ketone, such as cyclopentanone, cyclohexanone, or other alicyclic ketones having up to 10 carbon atoms. The lower alcohol is preferably present in an amount from 10 to 50 percent by weight of the composition and the lower ketone is present in the amount of 50 to 10 precent by weight of the composition.

The amount of carrier employed usually is in the range of about 40 to about 90 percent by weight of the composition, and in the preferred practice is in the range of about 65 to about 85 percent by weight of the composition.

Suitable colourants include carbon black and dye-stuff components that are soluble or dispersable in the solvent, such as solvent black 7 and solvent blue 36 dyes. Preferred solvent black 7 dyes are typically selected from dyes such as ATLASOL spirit nigrosine B base. One skilled in the art will be able to ascertain other such operable dyes through reference to information as contained in the Colour Index Guide.

The amount of colourant employed in the practice of the invention is not critical and can be varied within relatively broad ranges. In general, the colourants are present in the composition in amounts varying from about 0.5 to about 5 percent and preferably from about 1.5 to about 2.5 percent, based on the weight of the ink compositions.

Suitable conductivity control components which optionally may be present include, among others, soluble ionizable salts such as alkali metals and alkaline earth metal halides, nitrates, thiocyanates, acetates, propionates, and amine salts. An example of such salts is lithium nitrate. The salts are typically used in an amount of 0.1 to about 2 percent by weight of the composition and preferably from about 0.3 to about 0.8 percent by weight.

While not essential to the practice of the present invention, the ink composition of this invention can also be formulated to include evaporation retardants for the purpose of retarding evaporation of the solvents. Such retardants are a drying control component and are conventional in ink jet printing compositions. Typical evaporation retardants include glycol ethers, glycol esters or combinations thereof. Especially preferred is diethylene glycol monoethyl ether.

The evaporation retardant typically is present in an amount up to about 10 percent by weight based on the weight of the composition, and preferably from about 2 to about 4 percent by weight.

As will be appreciated by those skilled in the art, the ink composition of the present invention also may be formulated to include one or more surfactants to impart desirable characteristics to the liquid ink composition. Preferred surfactants include non-ionic surfactants such as fluorinated alkyl esters such as "FLUORAD FC 430".

The jet printing ink composition may also contain various other optional components such as resistivity control agents to adjust the electrical resistivity of the ink. Electrolytes can be added to adjust the specific resistivity of the ink. Usable electrolytes include dimethylamine hydrochloride and hydroxylamine hydrochloride.

It also may be desirable to add humectants, such as ethylene glycol or propylene glycol methyl ether, to prevent the ink jet tip from drying. Small amounts of organic cosolvents may also be added to improve drying time and reduce surface tension. Suitable cosolvents include n-methyl-2-pyrrolidone and butanol. Other conventional components may also be employed in the jet printing ink compositions.

In practice, jet printing ink composition may be applied to several different types of substrates, such as paper, glass, metal, and plastic.

In general, the ink compositions of the present invention exhibit the following characteristics for use in ink jet printing systems: (1) a viscosity from about 1.6 to about 7 centipoises (cps) at 25 • C, (2) an electrical resistivity from about 50 to about 2,000 ohms-cm, (3) a sonic velocity from about 1,200 to about 1,700 m/s to ensure proper nozzle resonance, and (4) a surface tension below 28 dynes/cm.

Inks of particular utility in which the secondary amine corrosion inhibitors may be employed are those disclosed in U.S. Patent No. 4,892,775.

Having described the basic concepts of the invention, reference is now made to the following nonlimiting Examples which are illustrative of ink compositions according to the present invention which are effective in ink jet printing onto various substrates.

EXAMPLE 1

	%
Methyl Ethyl Ketone (carrier)	39.35
Methanol (carrier)	24.63
Dimethylamine HCl (electrolyte)	0.8
H8-370 Polymer (Videojet Systems)*	26.72
Propyleneglycolmonomethyl Ether (humectant)	4.1
FC430 (In 10% MEK) (3M Co.) (surfactant)	0.9
Plasticizer 8 (Monsanto) (plasticizer)	0.5
Solvent Black 7 (Atlantic Dye Co.) (dye)	2.0
Diethylamine (Aldrich) (inhibitor)	1.0
	100.00

* H8-370 Polymer (Videojet Systems) is described in detail in U.S. Patent No. 4,834,799.

When the jet printing ink composition of Example 1 is placed into contact with stainless steel plates and printer parts, substantially no corrosion results whereas an otherwise identical composition, but not containing the diethylamine, causes deep pits and significant degradation of the stainless steel to occur.

EXAMPLE 2

	%
Methylethyl Ketone (carrier)	38.1
Methanol (carrier)	28.5
Hydroxylamine Hydrochloride (electrolyte)	1.0
Joncryl 67 (Johnson Co.) (binder resin)	4.0
Varcum 8357 (BTL Co.) (phenolic resin)	13.0
Propylene Glycol Methyl Ether (humectant)	5.0
N-Methyl-2-Pyrrolidone (cosolvent)	2.0
Santicizer 8 (Monsanto) (plasticizer)	2.0
FC-430 (3M Co.) (surfactant)	1.0
BYK 065 (defoamer)	0.9
Solvent Black 5 (Atlantic Co.) (colourant)	3.0
Diethylamine (Aldrich Corp.) (inhibitor)	1.5
	100.00

When the jet printing ink composition of Example 2 is placed into contact with stainless steel plates and printer parts, substantially no corrosion results whereas an otherwise identical composition, but not containing the diethylamine, causes deep pits and significant degradation of the stainless steel to occur.

Claims

1. A jet printing ink composition characterised in that it includes a sufficient quantity of at least one secondary amine selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, and dibutyl amine to inhibit the corrosiveness of the composition without adversely affecting its printing characteristics.

2. A jet printing ink composition comprising a carrier and a colourant that is soluble or dispersable in the carrier, characterised in that it includes a sufficient quantity of at least one secondary amine selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, and dibutyl amine to reduce the corrosiveness of the composition.

3. A jet printing ink composition, as in Claim 2, characterised in that it includes a resin binder that is soluble in the carrier.

4. A jet printing ink composition, as in Claim 2 or 3, characterised in that the carrier comprises a lower alcohol and a lower ketone.

5. A jet printing ink composition, as in Claim 4, characterised in that the lower ketone is selected from the group consisting of acetone, methyl isobutyl ketone, methyl ethyl ketone, cyclopentanone, and cyclohexanone.

6. A jet printing ink composition, as in Claim 4 or 5, characterised in that the lower alcohol is present in an amount from 10 to 50 percent by weight of the composition and the lower ketone is present in the amount of 50 to 10 percent by weight of the composition.

7. A jet printing ink composition, as in any of Claims 2 to 6, characterised in that it includes a conductivity control component and a drying control component.

8. A jet printing ink composition, as in Claim 7, characterised in that the conductivity control component comprises a soluble ionizable salt.

9. A jet printing ink composition, as in Claim 7 or 8, characterised in that the drying control component is selected from the group consisting of glycol ethers.

10. A jet printing ink composition, as in any preceding claim, characterised in that it has a viscosity from 1.6 to 7.0 cps at 25 °C, an electrical resistivity from 50 to 2000 ohms-cm, a surface tension below 28 dynes/cm, and a sonic velocity ensuring proper nozzle resonance of 1200 to 1700 m/sec.

11. A jet printing ink composition, as in any preceding claim, characterised in that the secondary amine or amines comprise between 0.1 percent and 10 percent by weight of the composition.

12. A jet printing ink composition, as in Claim 11, characterised in that the secondary amine or amines comprise between 0.5 percent and 2 percent by weight of the composition.

13. A jet printing ink composition, as in Claim 12, characterised in that the secondary amine or amines comprise between 1 percent and 1.5 percent by weight of the composition.

14. A jet printing ink composition, characterised in that it has the formulation of Example 1 and inhibits the corrosion of stainless steel plates and/or metal parts of ink jet printers.

15. A jet printing ink composition, characterised in that it has the formulation of Example 2 and inhibits the corrosion of stainless steel plates and/or metal parts of ink jet printers.

16. A method of producing a jet printing ink composition, characterised in that the corrosiveness of the composition to metal is reduced by adding a quantity of at least one secondary amine selected from the group consisting of diethyl amine, dipropyl amine, diisopropyl amine, and dibutyl amine , and the quantity of added secondary amine is insufficient adversely to affect the printing characteristics of the composition.

17. A method, as in Claim 16, characterised in that the quantity of secondary amine or amines is between 0.1 percent and 10 percent by weight of the composition.

18. A method, as in Claim 17, characterised in that the quantity of secondary amine or amines is between 0.5 percent and 2 percent by weight of the composition.

19. A method, as in Claim 18, characterised in that the quantity of secondary amine or amines is between 1 percent and 1.5 percent by weight of the compostion.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 1050

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 269 627 (KI-SUP HWANG) * column 3, line 65 - column 4, line 4 * * column 4, line 64 - column 5, line 2; claims 1,5,6 * -----	1,2,4,9, 16-18	C09D11/00
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 JUNE 1992	BUSCAGLIONE Y.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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